REACTIVITY OF TRI-GAS CHAR IN A FLUIDIZED-BED REACTOR

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INTRODUCTION

The evolution and the development of the BCR TRI-GAS fluidized-bed gasification process to produce low- to medium-Btu fuel gas has been described in two earlier papers.[1,2] TRI-GAS is a multiple fluidized-bed coal gasification process. The overall objective of TRI-GAS is the gasification of a range of coals, with the only product being a clean, low-Btu fuel gas. No liquids, tar, or char are produced as a waste or by-product. The process consists of three fluidized-bed reactors connected in series. Each reactor has its own specific function. Stage 2 is the main gasification stage. In this stage, devolatilized coal (char) and the volatile products from Stage 1 are gasified with air and steam, producing a low-Btu (about 150 Btu/cu ft) fuel gas.

The objective of the current study is to establish a model for the overall gasification reaction in a fluidized bed and to use this model to predict conversion in the TRI-GAS Stage 2 reactor during PEDU tests. The model assumes that the overall reaction rate is determined by the separate rates of two processes in series; first, mass transfer, where steam must be transported out of the bubble to the particulate phase, and second, the chemical reaction. The chemical reaction process has been isolated from mass-transfer effects and studied independently in the thermogravimetric analysis (TGA) unit where a chemical reaction rate is established, describing the resistance of the chemical process. Similarly, the tests in the bench-scale fluidized-bed reactor establish a parameter characterizing the mass transfer process from the bubble to the particulate phase.

APPARATUS AND PROCEDURE

Char Preparation

Char (+100 mesh) from the Rosebud seam coal pretreated during a typical PEDU test was used for reactivity studies in the TGA apparatus and the bench-scale fluidized-bed batch reactor. This char was produced by pretreating the Rosebud seam coal in a fluidized bed at 900 F to remove volatile matter and tars from the coal prior to feeding to the gasification reactor.

TGA Reactivity

An American Instrument Company basic thermogravimetric analysis unit was used for the reactivity measurements. About 100 mg of char contained in a ceramic pan was heated in nitrogen to the chosen reaction temperature. Since some devolatilization occurred during this process, heating continued until the char weight became constant. The nitrogen was then bubbled through water held at a specified temperature and this reactant passed over the char. Char weight loss was recorded continuously as a function of time.

The measure of reactivity chosen in this study was the same as Jenkins' "reactivity parameter".[3] The definition is (symbols defined in Appendix A):

$$R_5 = \frac{1}{W_o} \frac{dW}{dt}$$

The maximum rate of weight loss ($\frac{dW}{dt}$) was determined experimentally from the slope of the weight loss data recorded on an X-Y plotter. The maximum rate could be defined without difficulty since, in all cases, the initial rate was constant.

The reactivity parameter was assumed to depend on reacting gas concentration, C_p, in the following manner:

$$R_5 = k \quad C_p^n \tag{1}$$

where

$$k = \alpha \exp - \frac{E}{RT}$$

Taking the natural logarithm of both sides of Equation (1) results in

$$\ln R_5 = \ln k + n \ln C_p \tag{2}$$

A multiple linear regression analysis was performed using reaction rate (R_5) data taken at constant temperature for various values of C_p, resulting in values of n. The values of n, taken for several temperatures, were then averaged.

With n thus defined, Equation (1) can be used to determine the apparent activation energy and frequency factor for each reaction. Solving for k in Equation (1) results in

$$k = \frac{R_5}{C_p^n} \tag{3}$$

The right-hand side of this expression can be calculated from the data, the previously determined values of n, and the experimental conditions. Again, taking the logarithm of both sides results in

$$\ln k = \ln \frac{R_5}{C_p^n} = \ln \alpha - \frac{E}{RT} \tag{4}$$

A multiple regression analysis was performed using data at several temperatures resulting in the "apparent" activation energy E and the frequency factor α for each reaction. These results are reported in Table 1.

TABLE 1. TGA REACTIVITIES AND KINETIC PARAMETERS OF CHAR USED IN LABORATORY STUDIES

Test No.	Sample Temp, °K	Volatile Matter, mg	Steam Concentration, moles/cu cm	Reactivity, $(hr)^{-1}$
1	1193	12.8	0.89×10^{-6}	2.21
2	1193	13.3	1.35×10^{-6}	3.11
3	1193	13.5	2.01×10^{-6}	3.76
4	1136	11.5	0.93×10^{-6}	1.67
5	1136	12.0	1.42×10^{-6}	2.12
6	1136	11.5	2.11×10^{-6}	2.67

$$R_5 = C_p^n \quad \alpha \exp^{-E/\bar{R}T}$$

$$n = 0.61$$

$$\alpha = 1.94 \times 10^7$$

$$E = 17{,}662 \text{ cals}$$

Fluidized-bed Reactor

A schematic of the bench-scale fluidized-bed pressurized batch reactor system is shown in Figure 1. This system can be used for reactivity analysis with steam, carbon dioxide, and air. The reactor is made of 5.08 cm diameter by 91 cm long Incoloy 800 pipe. The reactor furnace consists of two 1450 watt, 61 cm long, furnace half-sections. The steam is generated by bubbling the inert gas through a 10.16 cm diameter by 51 cm long 316SS water-filled vessel heated by 2KW immersion heater. This steam generator is capable of producing saturated steam at 150 psi pressure. The reactor is followed by a water-cooled vessel where condensibles can be collected. The precise metering of the reacting gases is accomplished through Brooks Instrument Model 1110 rotameters. Foxboro pressure and DP cell transmitters are used for pressure control in the system and differential pressure measurements in the bed. For efficient distribution of the reacting gases in the reactor, the grid system consists of a 5-cm fixed bed of Steatite packing, packed between two screens. The system is also equipped with necessary auxiliary equipment for indicating actual pressures and temperatures in the reactor and the boiler. The system can be used to generate the reactivity data at 2200 F temperature and 150 psi pressure.

A 200-gm sample of the char was heated to the chosen reaction temperature and pressure with nitrogen flowing through the bed. Then the water-vapor reactant was generated by bubbling the nitrogen through hot water at a specified temperature and passed through the reactor. After a specified period of time, the reaction was quenched when the bed was purged with nitrogen. Conversion was determined by weighing the sample after cooling.

In a fluidized-bed reactor, the experimental value of the percent unreacted char is given by:

$$Y_{exp} = \frac{W}{W_o} \times 100$$

THEORETICAL MODEL

The model assumes that the overall reaction rate is determined by the separate rates of two processes in series; first, mass transfer, where steam must be transported out of the bubble to the particulate phase, and second, the chemical reaction. The chemical reaction process has been isolated from mass-transfer effects and studied independently in the thermogravimetric analysis (TGA) unit where a chemical reaction rate constant describing the resistance of the chemical process was established.

The following development is essentially that presented by Orcutt.[4] Only the detailed form of the reactant conversion term (R_c) differs. The form used in this study was developed empirically from differential reactor (TGA) data. The fluid bed is assumed to be divided into two distinct phases called the bubble and particulate phase. The reactant flow above that required to just fluidize the bed forms the bubble phase. No solids exist in this phase so no chemical reactions can occur. It is assumed that the bubble size is uniform. The particulate phase consists of the remainder of the flow and the solid char. The char-steam chemical reaction occurs in the particulate phase. Furthermore, the turbulent action in the bed allows the assumption that the steam concentration and temperature are constant throughout the particulate phase.

A material balance on a single rising bubble gives:

$$U_B V \frac{dC_B}{dy} = Q\,(C_P - C_B) \qquad (1)$$

Since C_P is assumed to be a constant, Equation (1) can be integrated directly to obtain:

$$\int_{C_O}^{C_B} \frac{dC_B}{C_P - C_B} = \frac{Q}{U_B V} \int_0^y dy$$

$$C_B = C_P + (C_0 - C_P) \exp^{-X(y)} \tag{2}$$

where $$X(y) = \frac{Qy}{U_B V}$$

The particulate phase material balance is:

$$R_1 + R_2 = R_3 + R_4 + R_5 \tag{3}$$

The amount of reactant transferred from the bubble, R_1, is determined by integrating the flow from the individual bubbles to the particulate phase over the entire reactor:

$$R_1 = A_T\, NQ \int_0^L C_B\, dy$$

Using Equation (2) for C_B results in:

$$R_1 = A_T\, NQ \left[C_P L - (C_0 - C_P) \frac{U_B V}{Q} \exp^{-X(L)} + (C_0 - C_P) \frac{U_B V}{Q}\right] \tag{4}$$

The amount of reactant fed directly to the particulate phase is:

$$R_2 = A_T\ U_{mf}\ C_0 \tag{5}$$

and leaving the particulate phase is:

$$R_4 = A_T\ U_{mf}\ C_P \tag{6}$$

The amount of reactant transported from the particulate to the bubble phase is given by:

$$R_3 = A_T\, NQ\, L\, C_P \tag{7}$$

Finally, the reactant consumed by the gasification reaction in the particulate phase is given by:

$$R_5 = A_T\, L_{mf} \left(\frac{1}{V_{TMF}} \frac{dN_R}{dt}\right) \tag{8}$$

The TGA data are used to evaluate the right-hand side of Equation (8). The TGA reaction rate is given by:

$$\frac{1}{W_o}\ \frac{dW}{dt} = -k\ C_P^n\ \frac{W}{W_o} \tag{9}$$

But,

$$dW = M_C\ dN_C$$

Thus,

$$\frac{dN_C}{dt} = -\frac{W_o}{M_C}\ k\ C_P^n\ Y$$

For the reaction:

$$C + H_2O \longrightarrow CO + H_2$$

$$\frac{dN_C}{dt} = \frac{dN_R}{dt}$$

so that,

$$\frac{1}{V_{TMF}}\ \frac{dN_R}{dt} = -\frac{W_o}{M_C\ V_{TMF}}\ k\ C_P^n\ Y \tag{10}$$

Substituting this expression into Equation (8) gives:

$$R_5 = \frac{A_T\ L_{mf}}{V_{TMF}}\ \left(\frac{W_o}{M_C}\right) k\ C_P^n\ Y \tag{11}$$

Substituting Equations (4), (5), (6), (7), and (11) into Equation (3) gives:

$$(VNU_B)\ (C_O - C_P)\ (1 - \exp^{-X(L)}) + U_{mf}\ (C_O - C_P) = \frac{1}{A_T}\ \frac{W_o}{M_C}\ k\ C_P^n\ Y$$

From Reference 6

$$VNU_B = U_o - U_{mf}$$

and defining:

$$\beta = 1 - \frac{U_{mf}}{U_o}$$

$$\xi_P = \frac{C_P}{C_O}$$

and

$$\lambda = \frac{W_o}{M_C} \frac{k\, C_o^{n-1}}{A_T\, U_o}$$

the nondimensional form for the particulate phase balance becomes,

$$(1 - \xi_p)\ [\beta\ (1 - \exp^{-X(L)}) + (1 - \beta)] = \lambda\ Y\ \xi_p^n \ . \quad (12)$$

In nondimensional form, Equation (9), describing the char conversion, becomes:

$$\frac{dY}{d\tau} = - \gamma\ \xi_p^n\ Y \quad (13)$$

where

$$\tau = \frac{t}{t_R}$$

$$\gamma = k\ C_O^n\ t_R$$

To compare this model with data from the batch laboratory tests, Equation (13) is integrated numerically to determine char weight for various run times. For each integration step, Equation (12) is solved for ξ_p.

RESULTS AND DISCUSSION

The results of the char conversion experiments at atmospheric pressure are shown in Figure 2. Also shown on this figure are the theoretical conversions predicted using transfer parameters (X) calculated from the Kunii and Levenspiel (K&L)[5] and the Davidson and Harrison (D&H)[6] models. Reactivities determined from TGA tests (Table 1) were used in the theoretical conversion calculation. In both models, average bubble size was calculated from Mori and Wen[7] and the self-diffusion coefficient calculated as in Reference 8. Both theories overpredict the char conversion. Actual conversion corresponds to a mass-transfer parameter X = 0.75 as opposed to X = 1.79 predicted by K&L and X = 4.73 predicted by D&H, Table 2.

TABLE 2. MASS TRANSFER PARAMETER, X, FOR CHAR USED IN LABORATORY TESTS

Reactor Pressure, psia	U_o/U_{mf}	Kunii & Levenspiel	Davidson & Harrison	Experimental	Gas Diffusivity D_g (adjusted) cm^2/sec
14.7	9.34	1.79	4.73	0.75	0.52
70.0	3.78	1.99	5.78	0.08	0.0008

Examination of the expressions used to calculate X from both models reveals two parameters that can be adjusted to allow agreement between the experiment and the theory. These are the bubble diameter (D_B) and the gas self-diffusion coefficient (D_g). The bubble diameter would have to be adjusted to about 10 cm to allow X = 0.75. Since this is considerably larger than the reactor (D_T = 5.08 cm), it is necessary to adjust D_g. Adjusting D_g from a theoretical value of D_g = 3.33 cm^2/sec down to D_g = 0.52 cm^2/sec and using the Kunii and Levenspiel model results in X = 0.75 and agreement with the experimental data. The conversion results at 70 psia are shown in Figure 3. The experimentally determined X and D_g adjusted to achieve this X at 70 psia are shown in Table 2.

It is interesting to note that to achieve these low transfer parameters, models must be employed with more than one transfer resistance in series. One of the resistances must depend on gaseous diffusion. Figure 4 shows the comparison of mass-transfer parameters calculated using a simple resistance theory (D&H) and a three-resistance theory (K&L). In the D&H model, it is assumed that two transfer mechanisms are occurring in parallel. There is a macroscopic movement of gas from the bubble along with a microscopic diffusive transfer. As D_g goes to zero, the D&H model predicts that X approaches a finite value ($X \simeq 0.5$)^g dependent only on the macroscopic transfer between the bubble and particulate phase. Calculation as D_g goes to zero at the elevated pressures results in about the same value for X. Since this is substantially greater than the experimental X, a theory incorporating a totally diffusive resistance in series must be used.

The K&L theory assumes the same transfer mechanisms as D&H out of the bubble, but places a third resistance, namely the cloud, between the bubble and the particulate. The transfer through the cloud is only due to gaseous diffusion. Thus, for the K&L case, the diffusive transfer between the cloud and the particulate phase can choke off the flow and the overall coefficient between bubble and particulate can be adjusted as low as needed to agree with experiment.

SUMMARY OF RESULTS

1. A two-phase fluidized-bed model can be used to predict the conversion observed in the char-steam gasification reaction in a 5.08-cm fluidized-bed reactor.

2. The best fit of the experimental data was obtained using the K&L model to calculate the mass exchange between the bubble and particulate phases.

ACKNOWLEDGMENT

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APPENDIX A

NOMENCLATURE

A_T = Reactor cross-sectional area, sq cm

C_O, C_P, C_B = Steam concentration in reactor inlet, particulate phase and bubble phase, moles/cu cm

D_g = Gas Diffusivity, sq cm/sec

D_T = Reactor diameter, cm

k = Reaction rate constant

L, L_{mf} = Fluid bed height, height at minimum fluidization, cm

M_C = Char molecular weight, gm/gm mole

n = Exponent for char reactivity

N = Number of bubbles per unit volume, 1/cu cm

N_C, N_R = Number of reacting moles of char and steam

Q = Effective volumetric flow rate from the bubble phase to the particulate phase, cu cm/sec

R_1, R_2, R_3, R_4, R_5 = Reactant transported from the bubble to particulate phase, fed to particulate phase, transported from the particulate to bubble phase, left the particulate phase and disappeared due to chemical reaction in particulate phase, moles/sec

S = Surface area of the rising bubble, sq cm

t, t_R = Time, solids residence time, sec

U_o, U_B, U_{mf} = Superficial velocity, bubble velocity, minimum fluidization velocity, cm/sec

V, V_P, V_{TMF} = Bubble volume, particulate phase gas volume, total fluid bed volume at minimum fluidization conditions, cu cm

W, W_o = Instantaneous char weight, weight at the instant the reacting gas is introduced (on ash-free basis), mg

X = Mass transfer parameter

y = Axial distance from the reactor inlet, cm

Y = W/W_o

α = Frequency factor

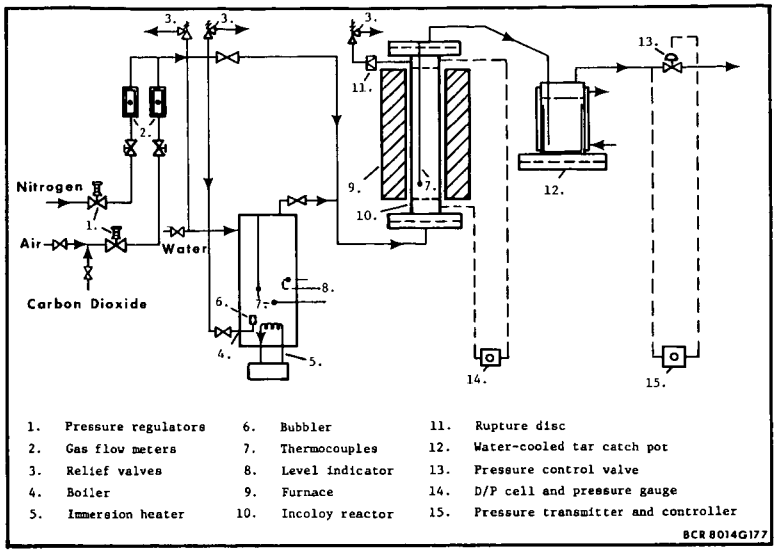

Figure 1. Flow Diagram of Laboratory Fluidized-bed Test Unit

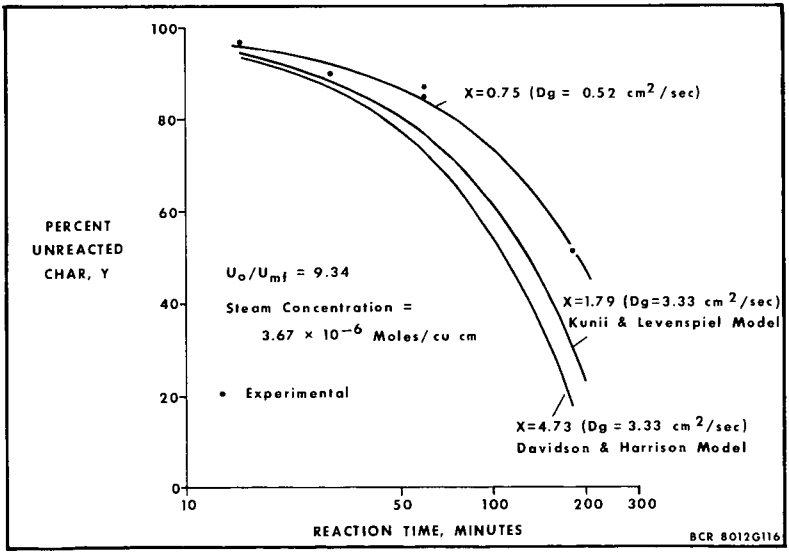

Figure 2. Char Conversion at Atmospheric Pressure and 1800°F Temperature

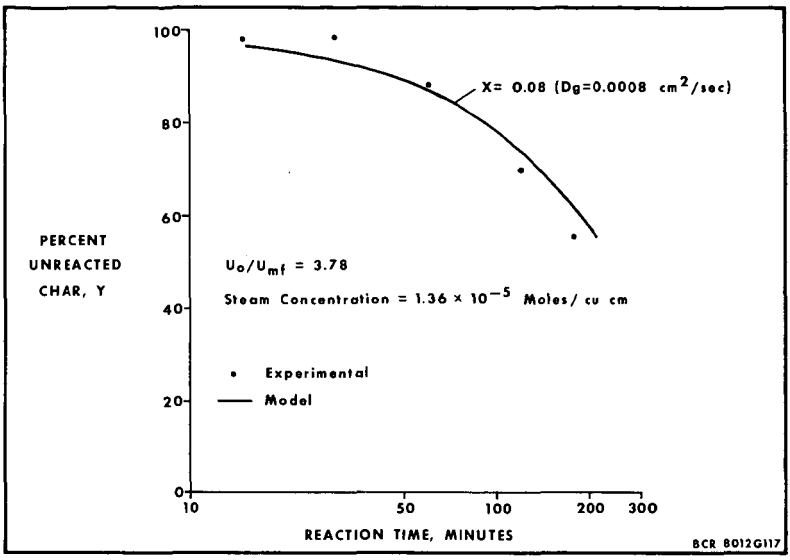

Figure 3. Char Conversion at 70 psia Pressure and 1800°F Temperature

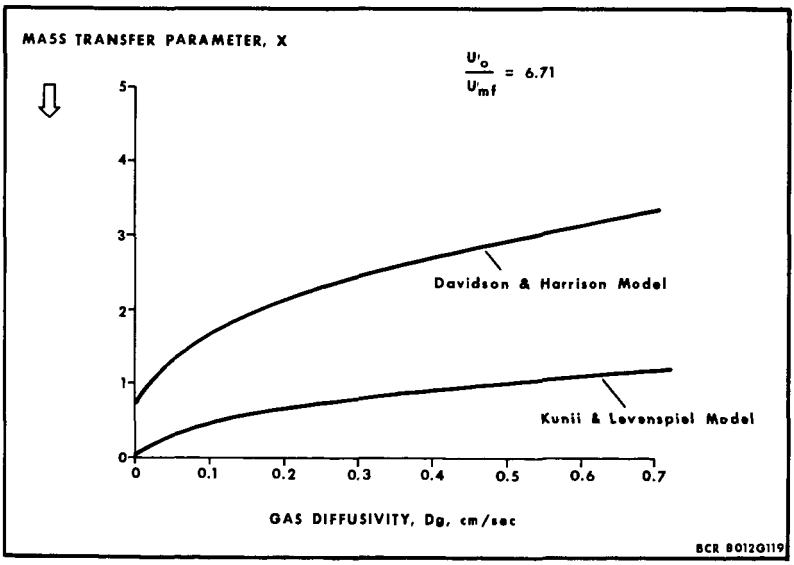

Figure 4. Diffusivity Effect on the Mass Transfer Parameter in a Fluidized-bed